IN RE: U.S. Serial No. 10/523,708
FOR: TRANSMISSION BELT
INVENTOR: SATO, Yoshitaka et al.
ASSIGNEE: Gates Corporation
DOCKET NO: GUA UTO318

DECLARATION

I, Paul N. Dunlap, under penalty of law hereby declare as follows:

1. I reside at 6283 S. Galena Way, Englewood, CO 80111, United States.

2. In 1978 I obtained a Bachelor of Science degree in Chemical Engineering with special honors from the University of Colorado. In l981 I was awarded Master of Science and in 1986 Doctor of Philosophy degrees in Chemical Engineering from California Institute of Technology. I have six refereed publications in the fields of polymer solution rheology and composites, and am named as an inventor on two U.S. patents (U.S. Pat. Nos. 7,078,104 and 7,166,678) and on two patent applications pending before the USPTO.

3. From 1986 – 1990 I was employed at Corning, Incorporated where I conducted research on glass/polymer composites.

4. From 1990 until late 2003 I was employed by The Gates Corporation, assignee of the captioned patent application, in their power transmission belt division. My focus at Gates prior to late 2003 has been in belt development and materials research (for belts), which has led to commercialization of new products and the engineering of production processes. I have dealt with a wide variety of power transmission belts and elastomeric compositions at Gates including fiber-loaded compositions for reinforced rubber belts. I am quite familiar with Gates' commercial line of automotive and industrial rubber belts on the one hand (V-type, V-ribbed and synchronous), and polyurethane belts on the other (V-type and synchronous), and their methods of production.

5. From late 2003 through 2005, I was employed by The Gates Corporation half time as a Patent Agent, having become registered in early 2003. At the same time I attended law school and was award the Juris Doctor degree in December 2005 by the University of Colorado-Boulder School of Law. I have been employed full time as Patent Counsel by Gates since 2006, USPTO registration number 52,840. I have written and prosecuted a number of patent applications relating to fiber-loaded v-belts and multi-v-ribbed belts, drawing on my past experience with Gates.

6. I have been asked to comment, as an expert in the field of rubber compounding for belts, on the results presented in U.S. Patent Application 10/523,708 – in particular, whether the results in Figures 3 and 4 are unexpected. In my opinion, certain results in Figures 3 and 4 are unexpected. I base this on three separate approaches: (1) the general nature of the short-fiber reinforced rubber ("SFRR") composite; (2) predictions based on theoretical and empirical models; and (3) the empirical trends found in the data of Figures 3 and 4.

<u>(1) General nature of SFRR.</u>

7. Short-fiber reinforced rubber composites are generally known to be unpredictable in certain physical properties. One such unpredictable property is tensile strength. While composite modulus is generally predictable from a knowledge of the rubber matrix and fiber moduli, the fiber concentration, and the fiber dimensions and orientation, composite tensile strength depends on these plus a number of additional factors which are extremely unpredictable. Tensile strength depends, in addition, on the strength of the matrix and fiber, the degree of fiber dispersion, the extent of fiber interaction, stress concentrations, the matrix wetting of the fiber, and the matrix adhesion to the fiber, i.e., the interfacial bond strength. The unpredictability arises in large part from the dependence of fiber dispersion and fiber length on the mixing or other processing conditions applied to the composite. *See e.g.*, Lloyd A. Goettler, "Short-Fiber Rubber Composites," at Table 2 and p. 241, 244, in Anil K. Bhowmick & Howard L. Stephens, eds., "Handbook of Elastomers: New Developments and Technology," Marcel Dekker, NY, pp. 215-248 (1988) ("It is of interest that the tensile strength of discontinuous composites is not in proportion to the corresponding strength of the reinforcing fibers themselves. Other parameters relating to the composite structure are of greater consequence (see Table 2)." Goettler describes a number of examples in the literature where composite strength results are contrary to expectation, or non-linear, or more dependent on processing than on physical properties. *Id.* at p. 242. Indeed, in a more recent edition of the same book, the author focuses on the dominant relationship between processing and structure and the resulting effects on physical properties. Lloyd A. Goettler & William F. Cole, "Short Fiber-Filled Rubber Composites," in Anil K. Bhowmick & Howard L. Stephens, eds., "Handbook of Elastomers," 2d ed., Marcel Dekker, NY, pp. 241-264 at p. 241 (2001).

8. In this case, the general unpredictability of composite tensile strength is implicitly seen in the specification of the captioned patent application. The inventors make a valiant attempt to explain the mechanism of the invention in terms of processing conditions, degree

of dispersion, fiber orientation, and fiber properties (page 6-7). On one hand, these explanations are very qualitative, hand-waving arguments. On the other hand, these explanations are entirely consistent with the general state of the art regarding our understanding of how short-fiber rubber composites work. In short, the tensile strength of a unique combination of fiber materials and lengths is best determined by experiment and explained by hindsight reasoning, not predicted from first principles.

(2) Theory.

9. The theoretical models used for short-fiber reinforced rubber composites ("SFRR") have been described in various references, but fall very short of rendering tensile strength predictable. *See e.g.*, L.A. Goettler & K.S. Shen, "Short Fiber Reinforced Elastomers," Rubber Chem. & Tech., v. 56, pp. 619-638 (1983); S. Abrate, "The Mechanics of Short-Fiber-Reinforced Composites: A Review," Rubber Chem. & Tech., v. 59, pp. 384-404 (1986); M. Fukuda, T. Shioyama, & Y. Mikama, "V-Belt and Fan Belt Manufacturing Technology," in A.K. Bhowmick, M.M. Hall, & H.A. Benarey, eds., "Rubber Products Manufacturing Technology," Marcel Dekker, NY, pp. 593-649 (1994). What each of these reviews discusses is the rather successful theoretical modeling of modulus, and in contrast, the rather limited modeling of **strength** of rubber composites. The available theoretical predictions for tensile strength of SFRR may be summarized as follows. Tensile strength is expected to initially decrease as volume fraction fiber loading increases at very low loadings, reaching a minimum. (*See e.g.*, Abrate, p. 398). Then tensile strength is expected to increase until a critical loading is reached (Abrate, at p. 398, relates a measured critical loading of 10 phr in one study) beyond which strength of the composite is greater than the rubber matrix alone, but only if good bonding exists. The critical loading depends on fiber length. (Goettler, p. 241). Whether, the predicted behavior is observed in a given experiment depends on degree of bonding between fiber and matrix, and of course the degree of orientation and dispersion. (*Id.*). Theoretically, the tensile strength will approach a maximum value as fiber length increases, orientation is complete, and bonding is perfected. (Abrate, p. 386; Goettler & Shen, p. 628). Stronger fibers are expected to require a longer length to reach maximum strength in the composite, which will be a higher strength than with a weaker fiber. (*See* Abrate, p. 399). In blends of different fiber types, expectations are that the longer type tends to dominate the strength, unless it cannot be dispersed, oriented, or bonded as well as the shorter type, (noting that it is more accurate to compare based on length-to-diameter ratio). (*Id.*) One quantitative approach (*see* Abrate, at p. 399, Eq. 46) treats the composite strength as a straight-forward

linear sum of the matrix and fiber contributions, however, the fiber contribution is reduced by two empirical efficiency factors (less than 1) to account for processing and bonding effects.

10. In the present case, the data is measured at certain fixed fiber lengths and loadings and in the same matrix, most likely at a loading at or above the critical loading. Assuming perfect orientation, dispersion, and bonding for all samples, the example with the greatest amounts of the longest and strongest fibers is expected to have the highest tensile strength. Conex aramid is generally about the same to a little lower in strength compared to polyester, but being finer has a greater length-to-diameter ratio at the same length. Thus, my expectation of the examples in Table 1 would be as follows. Examples G and H, having the longest fibers (2, 3, & 5 mm), would be expected to have the highest strength. Of the samples containing only 1-mm and 3-mm fibers, Comparative example 2 would be expected to have the highest strength, because Comparative example 2 has 20 total parts of 3-mm fibers. Example E would be expected to follow closely behind or perhaps be equivalent to Comparative example 2, because it has the next greatest amount of the 3-mm fibers (15 parts), and it also has 15 parts of the shorter fiber. Likewise Example F should have a little lower strength than Comparative example 2 because the 2-mm fibers in example F reduce the average fiber length. Then Example A should be slightly better than Example C, because of its greater average fiber length. Thus, of the examples compared in Fig. 3, Comparative example 2 would be expected to have the highest strength. The observed ranking, E & F > C > A > 1 > 2, is thus quite unexpected. Especially, the fact that Examples C, F, and A have greater strength than Comparative example 2 is a surprise.

<u>(3) Empirical results.</u>

11. Finally, considering the tensile strength data of the present application by itself, in light of known trends in SFRR properties, there are surprises. Comparing Comparative example 2 to Examples A, F, and C reveals two surprises. First, comparing Comparative example 2 to Example A & F, we see that shortening the length of the aramid fibers from 3-mm to 1-mm or 2-mm increases the tensile strength of the composite, contrary to my expectations. (Longer fibers, or greater average fiber length, are generally expected to give higher strength.) Second, comparing Comparative example 2 to Example C, we see that reducing the amount of 3-mm polyester fibers, and replacing them with shorter 1-mm aramid fibers at the same total loading also increases the tensile strength of the composite, contrary to normal expectations. (At the same total loading, the sample with longer average fiber length

should have higher strength. Note that even on the basis of length-to-diameter ratio, 1-mm aramid is "shorter" than 3-mm polyester.)

Conclusion

12. Thus, in my opinion, tensile strength of short-fiber rubber composites is not easily predicted and subject to many process-specific and material-specific uncertainties. Even in a related series of experiments, unexpected trends have been demonstrated in the literature. Theoretical approaches may be useful in hindsight to explain results, but are little use in predicting the strength of new combinations. (E.g., as stated in Abrate at 391, "the Halpin-Tsai equations, provide hindsight into the phenomenon of reinforcement by short fibers.") This particular case, where a blend of 1-mm aramid and 3-mm polyester fibers performs significantly better than a similar blend of just 3-mm fibers, is, in my opinion, another example of an unexpected and unpredictable result in rubber composite science.

13. I declare the foregoing, under penalty of perjury, to be true.

Date: 6-21-2007

Paul N. Dunlap

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Denver, Colorado

Handbook of Elastomers

NEW DEVELOPMENTS AND TECHNOLOGY

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7
Short Fiber-Rubber Composites

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1. INTRODUCTION

While elastomers and compounded rubbers possess desirable characteristics such as low modulus and a high degree of recovery after deformation, they frequently cannot be utilized in applications requiring these properties. Other design requirements for the part, in particular high ultimate stress, limited elongation under load, creep resistance, and high-temperature performance, may not be met. Thus, some type of reinforcement is required. This could be in the form of continuous cords or, more recently, discontinuous particles of high aspect ratio. Short fibers, which constitute the major portion of the latter class, are the subject of this chapter. Special categories such as flake (e.g., mica composites) are omitted.

Other chapters in this volume treat alternative means for improving the performance spectrum of rubbery polymers other than by reinforcement, such as by blending them with other polymers of different characteristics, filling them with particulates, especially carbon black, or altering their own molecular makeup.

1.1 Advantages in Comparison to Cord Reinforcement

It is certainly no secret that the rubber industry thrives on composites of the continuous cord variety, e.g., for belts and carcass components of tires. The advantages to utilizing the reinforcement in this manner are as follows:

The reinforcing members are loaded directly and efficiently by the forces applied to the part, negating concern about stress transfer through the rubber phase.

Bonding to the rubber phase, while important, is not critical in many applications (excluding, perhaps, dynamic ones).

The cord-rubber composite remains quite flexible, both parallel to the direction of major reinforcement and, more especially, in the normal

TABLE 2 Structural Parameters Affecting Composite Performance

Fiber concentration (both for its effect on reinforcement and on loss of rubbery properties, e.g., tack)
Fiber aspect ratio (length)
Direction and extent of fiber orientation
Degree of fiber dispersion
Matrix wetting of the fiber
Matrix adhesion to the fiber
Void content

addition, the bundle itself may be low in strength due to poor wetout, as mentioned above. Either phenomenon is undesirable, as it reduces the overall strength of the composite.

Wetout and the related phenomenon of adhesion directly determine the ultimate performance of the composite through their effect on the strength of the interface (signified by the variable τ^* in the equations developed later), except in the unlikely event that the matrix rubber itself is even weaker.

3.2 The Interfacial Region

The interface is of great current research interest because, while not well defined, it appears to exert a substantial effect on the composite properties. Two major issues concerning the interface are its physical dimensions and its role in effecting a bond between the fiber and matrix phases. As generally conceived, the interface is a region at least several molecular layers thick whose properties are intermediary between the fiber and matrix phases because of the peculiar restrictions on its molecular motion. For example, surface matrix molecules may be anchored to specific sites on the reinforcement by reaction or adsorption, may diffuse into it, or may be affected by it through an alteration to the adjoining matrix morphology (e.g., crystallinity). The interface may be principally composed of an additional constituent that is added to the composite as a bonding or wetting agent or as an interlayer. The former should interact strongly with both phases by mechanisms similar to those mentioned above in order to strengthen an otherwise incompatible boundary. Interlayers are special treatments intentionally coated onto the reinforcement, usually prior to its incorporation into the matrix, to provide a gradation in mechanical properties (principally the elastic moduli) across the interfacial region. This reduces stress concentrations that might otherwise lead to premature failure under load.

There is a direct relationship between the strength of the interfacial region and the tensile strength of the fiber-rubber composite. Figure 2 shows that in the absence of a strongly bonded interface, the matrix tears away from the fiber at low stress levels, thus losing the reinforcing effect. The stress experiences a maximum or a plateau at that yield point, and

between those properties of the fillers alone and those of continuous cord construction. The fiber aspect ratio (length/diameter) should be in the range of 100–200 for optimum effectiveness. Longer fibers (e.g., cut polyester and nylon) tend to tangle, while brittle fibers break during processing into aspect ratios below 50. Fillers unlike carbon black that do not wet and bond to the rubber phase cause a weakening of the composite while still contributing to its stiffness.

The principal role of the rubber matrix is to transmit the applied loads, through shearing strain, to the reinforcing fibers. Therefore it plays an important role in conjunction with the aspect ratio of the fibers (see Section 3.4). Furthermore, however, the matrix phase is instrumental in determining the transverse tensile strength (measured 90° to any predominant fiber directionality), some shear properties, and high-temperature performance.

The primary effects of short-fiber reinforcement on the mechanical properties of rubber composites include increased modulus (stiffness), increased strength (with good bonding at high fiber concentrations), decreased elongation at failure (with strong fiber-matrix bonding; otherwise a residual high elongation obtains while the unbonded fibers are pulling away from rather than reinforcing the rubber matrix), greatly improved creep resistance over particulate-filled rubber (including carbon black), increased hardness, and, at relatively low fiber level, possible improvements in cut, tear, and puncture resistance. Increase in strength and stiffness apply to green as well as vulcanized composites.

Viscosity is generally augmented, although the effect can be managed through proper compound formulation. Hysteresis and fatigue strength are improved when a comparison is made on the basis of equal stress but suffer when the deformation of the composite is instead stipulated. On the basis of constant energy input, the effect is modest. Since processability, handling, and physical properties deviate strongly at high fiber concentrations, a low reinforcement level is often optimum in many applications.

O'Connor (1977) and Hamed and Coran (1978), among others, described the effects of fiber reinforcement on the properties, particularly tensile, of rubber stocks. When the fibers are well aligned parallel to the stress direction (termed "longitudinal orientation"), tensile strength develops a characteristic drop with increasing fiber volume content until a critical fiber level is reached. Higher reinforcement concentrations cause the strength to increase, but a plateau typically at two to three times the matrix strength begins to develop above about 30 vol % fiber. (See Fig. 7.) An initial drop in the tensile strength reaching a characteristic minimum around 5–10 vol % derives from the dilution effect of the fibers, which weakens the matrix if their concentration is not yet high enough to sustain the corresponding fraction of the tensile load. The critical concentration level at which the unreinforced matrix strength is recovered varies directly with the critical fiber aspect ratio. In the absence of fiber-matrix bonding, it is never reached.

It is of interest that the tensile strength of discontinuous composites is not in proportion to the corresponding strength of the reinforcing fibers themselves. Other parameters relating to the composite structure are of greater consequence (see Table 2). These are the length/diameter ratio (aspect ratio) of the fibers, which determines the extent of stress transfer into the reinforcing members; the degree of orientation and extent of fiber interaction (which are both influenced to some degree by fiber size and shape); interfacial bond strength; and the presence of stress concentrations

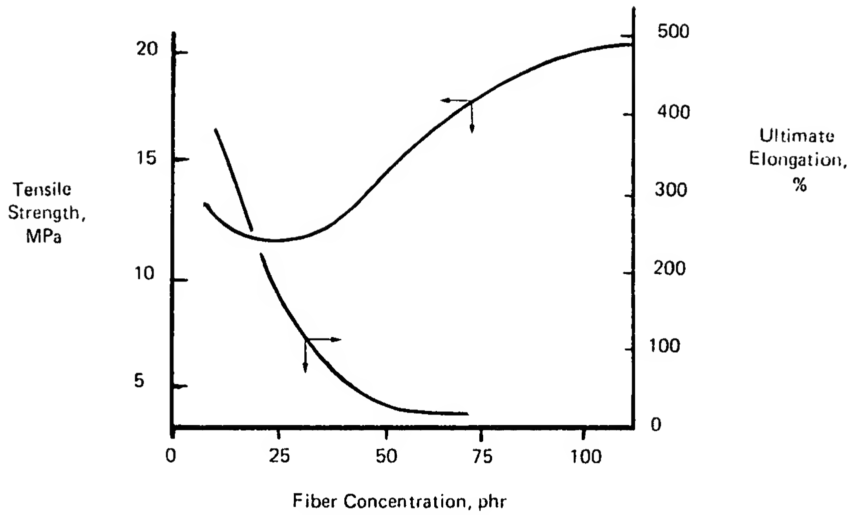

Fig. 7 Ultimate tensile properties in a well-bonded short fiber-rubber composite of high aspect ratio.

at the fiber ends and between fibers crossing or lying in close proximity to each other.

Thus, although short nylon reinforcing fibers are superior in terms of tensile strength, the weaker cellulose fibers (which, after all, comprise ordinary paper) actually yield a stronger rubber composite than glass, carbon, and even aramid fiber (O'Connor, 1977). Glass and carbon are deficient because their brittle nature results in a loss of aspect ratio during fabrication of the composite, while aramid fiber has been shown (Czarnecki and White, 1980) to buckle at regular short intervals rather than fracture.

The stiffness or modulus of a short-fiber composite increases monotonically with the fiber concentration up to a plateau at 30–40 vol %, above which structural defects become overriding. The functional dependence of the longitudinal Young's modulus is not necessarily linear in the volume percent fiber, as in the case of hard plastic matrices, however (Li et al., 1978). Nevertheless, strong increases almost in proportion to the fiber concentration are possible. Thus, with a cellulose fiber reinforcement, the Young's modulus of a typical rubber stock may be increased from 3 to >200 MPa.

Short fibers perform best when the composite is subjected to tensile rather than compressive strains. Fibers positioned parallel to a compressive load will buckle, thus losing their reinforcing potential. Consequently, the best compressional reinforcement is obtained with the fibers lying 90° to the stress direction, so that, by the Poisson effect, they are in a state of tension.

Fibers positioned perpendicular to a surface present the highest abrasion resistance but the least resistance to penetration. In either case, heightened penetration resistance produces higher hardness readings. Fiber reinforcement causes a loss of rebound elasticity, but it is not as detrimental as the use of high loadings of carbon black to increase durometer (hardness).

application of metal braids and can extend hose life by bridging the stresses across weakened filaments.

Diaphragms Short fibers increase stiffness and reduce extensibility; directional properties can be attained.

Gaskets Short fibers provide strength against blowout and reduce swell. If oriented in the plane, they allow thickness swell to improve sealing.

Tires Short fibers have the potential for reinforcing low-performance tires. In automotive and truck tires they find application in reducing cord shadowing in the innerliner, in stiffening of the bead filler, in better abrasion resistance for the chafer strip, and in improved cut resistance to treads, especially for trucks and OTR vehicles (Walker and Harber, 1985).

Sheeting Short fibers provide higher green strength and cut, tear, and puncture resistance. Some applications for such reinforced sheeting are in roofing membranes.

Energy management Short fibers can reinforce and stiffen rubber in fenders and other impact applications, in accordance with simple design equations.

Good dispersion of the short fibers within the rubber matrix is of prime consideration to obtain maximum performance in these applications. Therefore, fibers pretreated for improved mixing (as well as bonding to the rubber phase) are preferred. As indicated earlier, these considerations are perhaps of greater importance to design engineering than the mechanical properties of the short fibers themselves. Of course, thermal and environmental resistance continue to depend heavily on the material characteristics.

8. SUMMARY

While short-fiber composites have unique and useful properties, they are currently underutilized by the rubber industry. A singular advantage to this form of reinforcement is that the composite structure and properties can be optimized by manipulating the compounding and processing variables. Although the material costs may be nearly equivalent, lower manufacturing costs in comparison to cord constructions put short fiber rubber composites into a favorable cost-effective position. Beyond all current benefits, such short-fiber composites can serve to open up new vistas for the rubber industry.

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9
Short Fiber–Filled Rubber Composites

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1. ABSTRACT

This chapter covers the reinforcement of soft rubber matrices with short cellulose fibers. It focuses on the relationships of processing to structure and consequently to its effect on mechanical properties. The three most important structural parameters comprising fiber orientation, length, and degree of dispersion are considered. The first of these, fiber orientation, is determined predominantly by the geometry and flow in the forming operation used to produce the final part. On the other hand, the other two derive from an interaction of the material with the mixing process. Following some introductory remarks and a review of recent literature on short fiber–rubber composites, emphasis will be given to the effects of compounding on fiber length and dispersion and the resulting mechanical properties.

2. INTRODUCTION TO RUBBER COMPOSITES

The use of continuous cords for rubber reinforcement imparts high strength and stiffness in tension but produces little effect in compression and flexure. In many applications, e.g., tires, both continuous and discontinuous reinforcements may be required. They may either be incorporated in different components of the part or be combined together as a hybrid composite.

Another type of hybrid structure comprises the combination of short fibers with some type of particulate filler or reinforcement. In the rubber industry, carbon black is routinely employed to upgrade rubber properties. The small submicrometer size of these particles, even in aggregated form, in comparison to most short fiber dimensions, allow them to function independently of the presence of the larger discontinuous fiber reinforcement. Thus, short fiber composite mechanics simply considers them to alter the properties of the matrix rubber.

The real benefit to the short fiber reinforcement of any polymer, including rubber, lies in processing economics. Short fiber–rubber composites can be handled on conventional rubber-processing equipment, in sharp contrast to forms of continuous reinforcement (cord, fabric, etc.),

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SHORT FIBER REINFORCED ELASTOMERS*

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* Presented at a meeting of the Rubber Division, American Chemical Society, Chicago, IL., October -7, 1982.

gradient. Indeed, fibrous suspensions cease to behave as liquids if the fiber concentration or aspect ratio become excessive. By the controlled addition of glass fibers, efficient stiffening and thermal stability can be obtained without loss of fluidity or low temperature impact in RIM polyurethanes[95]. Different processing techniques are described by Isham[96,97] and Liedtke[98]. The types and concentrations of discontinuous fiberglass suitable for each process depends on the glass and polymer characteristics.

A novel processing technique for RRIM urethanes was introduced by Von Bramer, Baxter, and Douglas[99]. They demonstrate the feasibility of fabricating one-component urethane systems reinforced with 25 mm chopped glass fibers by conventional sheet molding compound (SMC) technology. The solid handling characteristics imparted by the long fiberglass along with solid chain extender and catalyst allow the use of simple compression molding presses in this processing technique developed for unsaturated polyester resin compositions. It circumvents the need for the expensive metering and mixing equipment of conventional RIM systems.

IV. DESIGN PROPERTIES

The mechanics of short fiber reinforced polymer composites, which include elastomeric matrices as a special class, are described in such classic texts as Broutman and Krock[100] or current ones as that by Folkes[101]. A good review of models for predicting the elastic moduli as a function of the shape of the reinforcing particle (including short fibers) is given by Chow[102]. Kardos[103] reviews theories on the strength of short fiber composites.

The mechanical properties of short fiber composites are intermediary between those containing continuous filaments or cords and particulate filled materials. This is particularly true of the responses in a direction parallel to that of the fibers when they are highly aligned. Transverse properties of short fiber composites would be nearly identical to those of their continuous fiber counterparts[104].

A portion of the literature on filled polymers, *i.e.*, those containing particulate solids, is also applicable to low aspect ratio fiber composites. A recent review of particulate fillers in elastomer reinforcement by Boonstra[105] is pertinent in this regard. Paipetis and Grootenhuis develop the dynamic properties of viscoelastic composites in companion papers dealing separately with particulate and (long) fiber reinforcements[106,107]. The effect of spheres is similar to that of fibers in the 90° direction in regard to increasing the damping capacity of the material. However, in the 0° direction, the fiber reinforced material becomes more elastic. Theoretical studies valid at low volume concentrations are confirmed by experimental data. The effects of the shape, size, and orientation of the fiber are studied. It should be noted that the composite displays a frequency-dependent response, *i.e.* it is viscoelastic, even when the components (matrix and reinforcement) are both purely elastic. This effect is attributed to the dynamic stress-strain fields that develop around the inclusions.

The mechanical properties of short fiber composites are determined by five parameters relating to the reinforcement: its length (especially in ratio to a diameter or minimum transverse dimension, called an aspect ratio), concentration, orientation, state of dispersion, and degree of adhesion to the matrix. These primary variables are in turn influenced by selection of the fiber and matrix type, presence of bonding agents and other compound additives that might interact with the fibers, and, perhaps most importantly, the processing conditions. The

THE MECHANICS OF SHORT-FIBER-REINFORCED COMPOSITES: A REVIEW*

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CONTENTS

I. INTRODUCTION

Short-fiber-reinforced composites have been used and analyzed for many years. While the mechanical properties of these have been studied extensively for structural components with rigid matrices, elastomeric composites have received relatively little attention.

In this review, the mechanical properties of short-fiber-reinforced composites and the factors that influence them will be examined. Emphasis will be placed on reinforced elastomer applications. Constitutive equations describing the stress-strain relations are introduced, and the stress distribution in a reinforcing fiber is discussed, along with its implications for the overall reinforcement. Micromechanics approaches allow elastic, viscoelastic, and strength properties of the composites to be predicted, given the properties of the constituents. While sometimes lacking accuracy, these methods offer great insight into the mechanism of reinforcement. Similar approaches are presented for cord-rubber and particle-filled composites for comparison.

II. CONSTITUTIVE EQUATIONS

Composite materials can usually be modelled as orthotropic materials for which the stress-strain relations are:

* Presented at a meeting of the Rubber Division, American Chemical Society, Los Angeles, California, April 23-26, 1985. B.

† Contribution No. 28.

The use of these transformation laws has been demonstrated for elastomeric composites[1,2].

III. THEORIES OF STRESS TRANSFER

In short-fiber composites, loads are transferred from the matrix to the fibers in a zone near the fiber end. In order to understand the mechanisms of short-fiber reinforcement, it is necessary to study the stress distribution around a fiber.

A well-known analysis of this problem is the shear-lag analysis of Rosen[5]. Several assumptions were made: the effect of adjacent fibers on the stress distribution is ignored and so is the effect of fiber-end geometry; the fiber stress is zero at the end and increases gradually as load is transferred from the matrix to the fiber. Maximum reinforcement would be achieved when fibers are long enough so that complete stress transfer occurs. When both fibers and matrix behave elastically, the minimum length δ for which this is achieved is:

$$\frac{\delta}{d} = \left[\frac{1}{2}\frac{E_f}{G_m}\frac{1 - v_f^{1/2}}{v_f^{1/2}}\right]^{1/2}, \tag{5}$$

where d is the fiber diameter, E_f fiber modulus, G_m the shear modulus of the matrix, and v_f is the fiber volume fraction. The minimum fiber aspect ratio decreases slightly with increasing fiber loading and is affected in a major way by the fiber-to-matrix modulus ratio. As shown in Figure 1, as E_f/E_m increases, the minimum aspect ratios become quite large. For example, when $E_f/E_m = 1 \times 10^5$, $\delta/d, = 430$. The minimum fiber aspect ratio required to obtain complete stress transfer is called the effective aspect ratio. Maintaining high fiber aspect ratio through processing is hard to achieve and, therefore, limits the efficiency

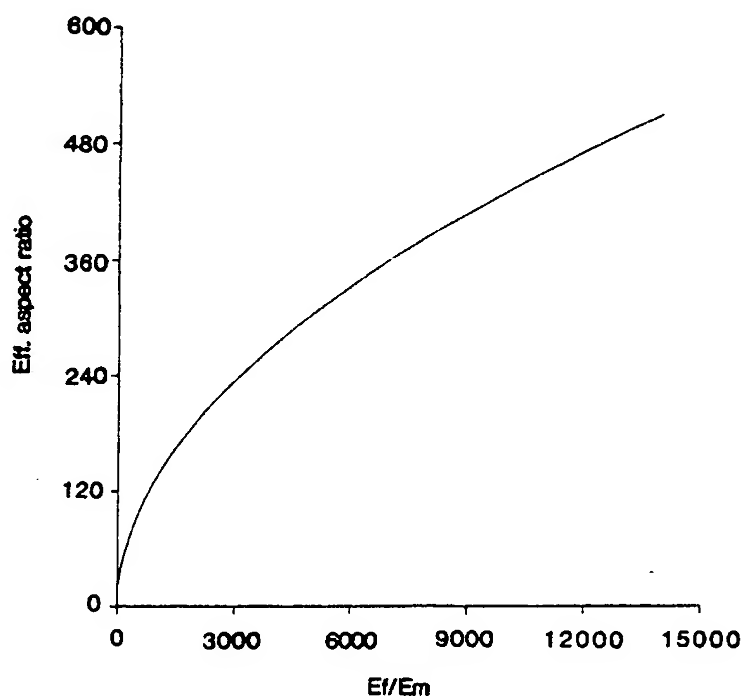

FIG. 1.—Effective aspect ratio as a function of fiber-to-matrix ratio.

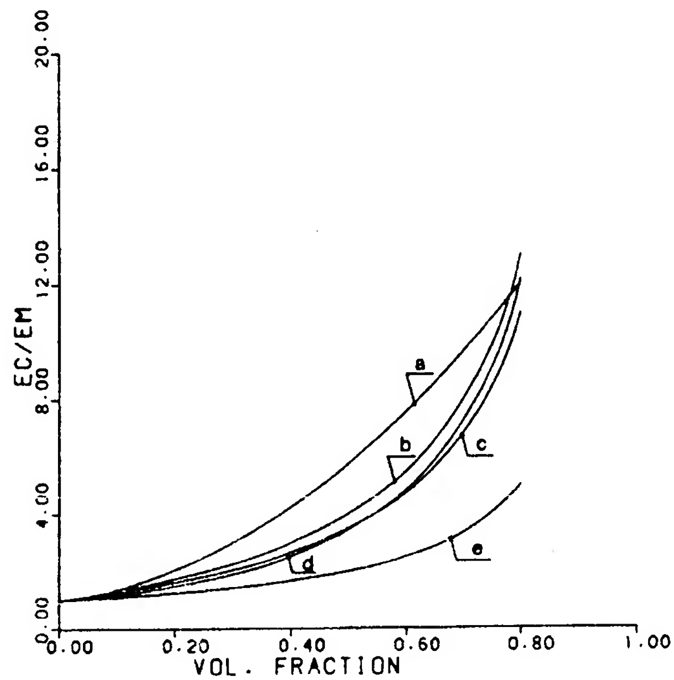

FIG. 2.—Variation of tensile modulus with filler volume fraction for particulate composites: (a) Equation (26), (b) Equation (20), (c) Equation (19), (d) Equation (14), (e) Lower Bound Equation (40).

The equations discussed above apply to the case of composite materials reinforced by rigid inclusions, and provide valuable estimates of elastic properties for small volume fractions.

C. SHORT-FIBER REINFORCEMENT

For short-fiber-reinforced composites, earlier analyses[20] predicted overall apparent elastic properties, neglecting the influence of the matrix. The following equations, called the Halpin–Tsai equations, provide hindsight into the phenomenon of reinforcement by short fibers:

$$\begin{aligned} E_1/E_m &= \left(1 + 2\frac{L}{d}\, n_L v_f\right)\Big/(1 - n_L v_f), \\ E_2/E_m &= [1 + 2n_T v_f]/(1 - n_T v_f), \\ G_{12}/G_m &= [1 + n_G v_f]/(1 - n_G v_f), \\ \nu_{12} &= \nu_f v_f + \nu_m(1 - v_f), \end{aligned} \tag{26}$$

where $$n_L = \frac{(E_f/E_m) - 1}{(E_f/E_m) + 2(L/d)},$$

$$n_T = \frac{(E_f/E_m) - 1}{(E_f/E_m) + 2},$$

$$n_G = \frac{(G_f/G_m) - 1}{(G_f/G_m) + 1}.$$

In this case, there are not enough fibers to control matrix elongation, and fibers would be subjected to high strains with only small loads and break:

$$\sigma_{c\ max} = \sigma_{m\ max}(1 - v_f). \tag{42}$$

For fiber loadings larger than V_{min},

$$\sigma_{c\ max} = \sigma_{f\ max}v_f + (\sigma_m)_{\epsilon f\ max}(1 - v_f) \tag{43}$$

and $\sigma_{c\ max}$ increases with fiber loadings. The minimum fiber loading is given by:

$$V_{min} = \frac{\sigma_{c\ max} - (\sigma_m)_{\epsilon f\ max}}{\sigma_{f\ max} + \sigma_{m\ max} - (\sigma_m)_{\epsilon f\ max}}. \tag{44}$$

For definition of variables, see Figure 8. The critical fiber concentration is defined as the fiber volume fraction for which composite strength is equal to the matrix ultimate strength.

$$V_{crit} = \frac{\sigma_{m\ max} - (\sigma_m)_{\epsilon f\ max}}{\sigma_{f\ max} - (\sigma_m)_{\epsilon f\ max}}. \tag{45}$$

Similar results hold true for short fiber composites[7], but, in that case, the situation is complicated by the influence of the fiber aspect ratio.

As shown in Figure 8, for low fiber loadings (v_f less than V_{crit}) the tensile strength of the composite is actually lower than that of the matrix. Experiments have shown this to hold true for short-fiber-reinforced elastomeric composites. A value for critical fiber loading of 10 phr was reported by Richard[14]. From

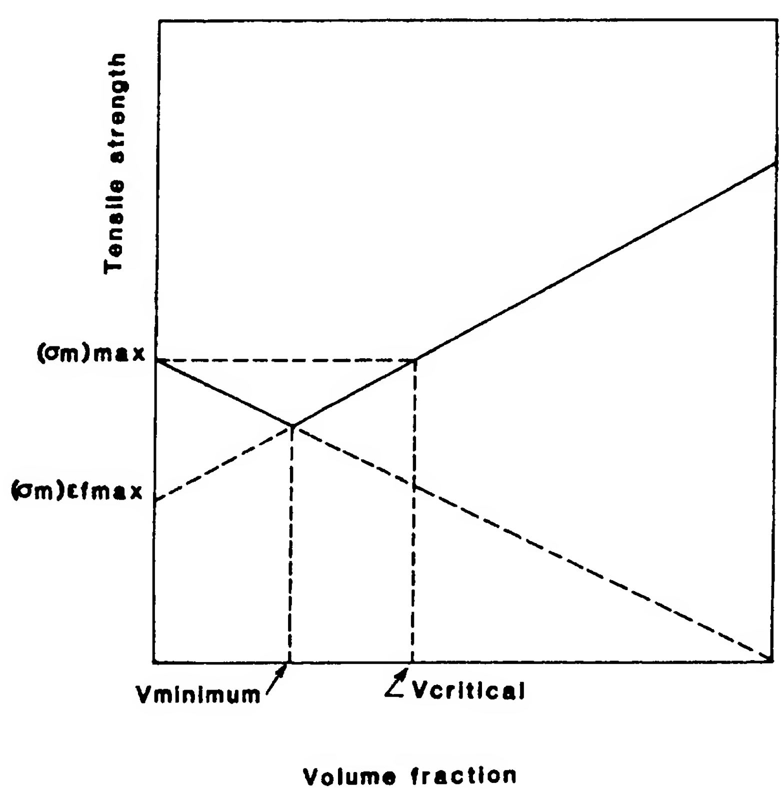

FIG. 8.—Variation of tensile strength with fiber volume fraction.

experiments conducted with low fiber loadings[34], it was stated that "the strength of the elastomeric composite is controlled by matrix properties," and that "use of short fibers in the reinforcement of rubber for the sole purpose of achieving higher strength becomes an exercise in futility." However, data on aramid and cellulose fiber reinforcement[34] (see Table I) supports the theory that composite strength first decreases for fiber loadings lower than V_{min} and remains lower than the matrix strain up to V_{crit}. The conclusions drawn from these observations can, therefore, apply only to subcritical fiber loadings where the behavior is indeed controlled by that of the matrix.

Similarly, for hybrid composites with high and low elongation fibers where the total fiber volume fraction is kept constant, tensile strength first decreases as the fraction of low elongation fibers decreases and high elongation fibers are introduced[38]. This is because the high elongation fibers are unable to carry the load when lower elongation fibers fracture.

Variations in fiber lengths affect the tensile strength of the composite. Because of the stress transfer mechanisms described above, shorter fibers develop low stresses and contribute less to the overall strength[38]. Analysis of a unit cell consisting of a central fiber and the surrounding matrix indicated that small deviations from loading along the fiber direction drastically reduce composite tensile strength[39]. One approach gives:

$$\sigma_c = \sigma_m v_m + v_f \sigma_f \epsilon_0 \epsilon_1, \tag{46}$$

where ϵ_0 and ϵ_1 are efficiency factors accounting for efficiency of reinforcement and fiber orientation respectively.

$$0 < \epsilon_1 < 0.95$$

and $\epsilon_1 = 1$ for uniaxially oriented fibers, 0.33 for random implane, and 0.162 for random 3-D orientation. Many other approaches have been presented[8].

In the transverse direction, the failure mode in the lamina form was found to be brittle fracture[40]. This implies that the controlling matrix property is the low elongation modulus rather than the elongation at failure.

For an orthotropic lamina with equal properties in tension and compression, there are three strength characteristics: the longitudinal strength X, the transverse strength Y, and the shear strength S[7]. Except for the three simple loading conditions of uniaxial longitudinal or transverse tension or shear, some biaxial strength theory has to be used. With the maximum stress condition, the stresses in the principal material directions must be less than their respective strengths. According to the maximum strain theory, the strains are now limited. A survey[41] of multiaxial strength criteria for composites describes the various approaches available.

TABLE I

TENSILE STRENGTH FOR TWO TYPES OF FIBER LOADINGS IN NEOPRENE[a]

	Fiber loading, % weight					
	0	1	3	5	10	15
Aramid	9.75	9.08	7.73	10.36		
Cellulose	9.75	—	—	7.65	6.22	6.99

[a] Tensile strength in MPa.